Redox Behaviors of Glassy Carbon Electrodes Modified with $[Fe_4X_4(YC_6H_4\text{-}p\text{-}t\text{-}C_4H_9)_4]^{2-}$ (X, Y=S and Se) in Water

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Cyclic voltammograms of glassy carbon electrode modified with iron–sulfur and iron–selenium clusters $(Bu_4N)_2[Fe_4X_4(YC_6H_4\text{-}p\text{-}t\text{-}C_4H_9)_4]$ (X, Y=S, Se) show the stable (2−/3−) redox couple in water, and the peak potentials of those redox waves are shifted by the change of pH due to reversible protonations not only of the oxidized but also of the reduced clusters. The electron transfer between the cluster and the glassy carbon plate is also influenced by the protonation equilibrium. A retardation of the electron transfer caused by the protonation of the cluster may be associated with a reorganization energy required in the redox reaction of the protonated cluster.

Synthetic Fe_4S_4 clusters with arene- and alkanethiolate ligands as models of 4Fe ferredoxins show reversible or pseudo-reversible $[Fe_4S_4]^{2+/+}$ redox couple not only in organic solvents but also in aqueous solutions.[1] On the other hand, some of biological redox reactions mediated by iron sulfur proteins involve a multi-electron transfer process such as NO_3^-[2] and SO_4^{2-}[3]-reductions, CO_2-assimilation,[4] and N_2-fixation.[5] Among those multi-electron reductions, N_2 fixation is especially interested in the viewpoint of the fact that N_2 is reduced with eight electrons to afford NH_3 and H_2, where unstable N_2H_2 is proposed as a reaction intermediate.[6] The construction of a catalytic system which can transport electrons rapidly to the reaction center, therefore, is desired in order to simulate multi-electron reductions involving unstable intermediates, otherwise the reaction intermediate may be decomposed without affording the final reduction product. In accordance with this view, six- and eight-electron reductions of RN_3 ($R=CH_2CH_2OH$) affording N_2H_4 and NH_3 via N_2H_2 can be achieved by using glassy carbon electrodes modified with $[Fe_6Mo_2S_8(SPh)_9]^{3-}$,[7] $[Fe_3MoS_4(SPh)_3(quinone)]_2^{4-}$,[8] and $[Fe_4S_4(SPh)_4]^{2-}$[8] under the controlled potential electrolysis at −1.25 V vs. SCE in H_2O, whereas the same clusters can catalyze only the two-electron reduction of RN_3 affording RNH_2 and N_2 under the electrolysis at the same potential in a homogeneous MeOH/THF solution. The superiority of the heterogeneous electrolysis to the homogeneous one with respect to a multi-electron reduction of RN_3 may be ascribed to an efficient multi-electron transfer to the cluster directly attached to the electrode in the former. Thus a multi-electron reduction involving unstable reaction intermediates can be achieved by a catalytic system which is provided with the ability of transport multi-electrons rapidly to the reaction center. On the basis of the fact that 4Fe ferredoxins mediate multi-electron transfer processes in biological reductions, synthetic Fe_4S_4 cluster modified electrodes may be applicable as redox catalysts to a wide range of reductions involving a multi-electron process. It seems, therefore, to be very important to elucidate the factor determining the rate of the electron transfer in the cluster-modified electrodes.

Experimental

General Procedure and Materials. All manipulations were carried out under N_2 atmosphere. Iron–sulfur and iron–selenium clusters $(Bu_4N)_2[Fe_4S_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ ($(Bu_4N)_4$-[4FeSS]), $(Bu_4N)_2[Fe_4S_4(SeC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ ($(Bu_4N)_2$[4FeSSe]), $(Bu_4N)_2[Fe_4Se_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ ($(Bu_4N)_2$ [4FeSeS]), and $(Bu_4N)_2[Fe_4Se_4(SeC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ ($(Bu_4N)_2$[4FeSeSe]) were prepared according to a literature.[9] Commercially available guaranteed reagents grades of NaOH and H_3PO_4 were used without further purification. Glassy carbon electrodes modified with a cluster (1×10^{-9}—1×10^{-6} mol cm^{-2}) were prepared by addition of a given amount of a CH_3CN solution of each cluster (1.0 mmol dm^{-3}) on a polished surface of the glassy carbon plates (1.0 cm^2) by syringe techniques and dried for ca. 30 min under dry N_2 stream.[7]

Physical Measurements. Cyclic voltammograms of cluster-modified electrodes were obtained at 298 K in H_2O by using a Hokuto Denko potentialstat HB-401, a Hokuto Denko function generator HB-107, and a Yokogawa Electric X-Y recorder 3077. H_3PO_4–NaOH was used as a supporting electrolyte in aqueous solutions.

Results and Discussion

Cyclic Voltammograms of Glassy Carbon Electrodes Modified with Clusters. It has been reported that Fe_4S_4 clusters attached covalently to a SnO_2 electrode[10] and incorporated in electrode-bound ion-exchange polymer[11] undergo a pseudo-reversible or reversible redox reaction in organic solvents. Compared with those Fe_4S_4 cluster-coated electrodes, the current cluster-modified electrode can be quite easily prepared. The cyclic voltammogram of the glassy carbon electrode modified with $(Bu_4N)_2[Fe_4S_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ ([4FeSS]/GC; 1×10^{-8} mol cm^{-2}) in water (pH 11.9) at 10 mV s^{-1} shows an anodic wave at −0.93 V vs. SCE together with a strong cathodic current at potentials more negative than −1.2 V due to not only the reduction of the cluster modified on the glassy carbon plate but also the evolution of H_2 catalyzed by the

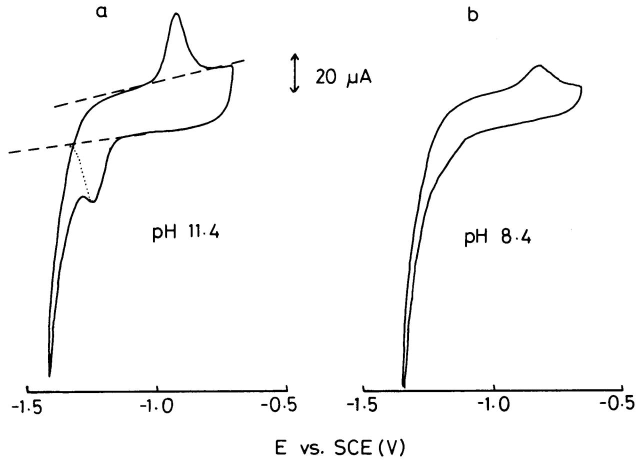


Fig. 1. Cyclic voltammograms of the glassy carbon electrode modified with $(Bu_4N)_2[Fe_4S_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ (1.0×10^{-8} mol dm^{-2}) in H_2O at pH 11.4 (a) and at pH 8.4 (b), $dE/dt=10$ mV s^{-1}; a dotted line (a) represents the pattern of the anodic wave.

reduced species of the cluster[12] (a solid line in Fig. 1a). The cyclic voltammogram of the [4FeSS/GC] was unchanged essentially even in a multi-scanning for 1 h. Thus, the Fe_4S_4 cluster modified on the GC plates stably undergoes a redox reaction in water. The cathodic wave at −1.24 V is almost superimposable on the anodic one at −0.93 V (a dotted line in Fig. 1a).[13] In addition, the electricity calculated from the area of the anodic wave corresponded to the number of $[4FeSS]^{2-}$ molecules modified on the electrode with the ratio of electron/molecule=1.00±0.02. These results clearly indicate that almost all the clusters undergo the $[4FeSS]^{2-/3-}$ redox reaction (Eq. 1) on the GC plate.

$$[Fe_4S_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{2-} + e^- \rightleftharpoons [Fe_4S_4(SC_6S_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{3-} \qquad (1)$$

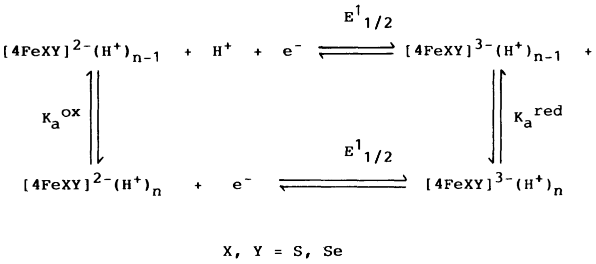
On the other hand, the change of pH of the aqueous phase from 11.4 to 8.3 causes a shift of the anodic wave from −0.93 to −0.82 V with decreasing the electricity of the wave at the same scanning rate (10 mV s^{-1}). At the same time, the cathodic wave was almost concealed by the anodic shift of the threshold potential of H_2 evolution (Fig. 1b). Such the change of the cyclic voltammogram of [4FeSS]/GC at pH 8.3 results from neither the decomposition nor stripping off the cluster from the GC plate since the cyclic voltammogram of [4FeSS]/GC at pH 11.4 was regenerated when the pH was put back to 11.4. The cyclic voltammograms of glassy carbon electrodes modified with $(Bu_4N)_2[Fe_4S_4(SeC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$, $(Bu_4N)_2[Fe_4Se_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$, and $(Bu_4N)_2[Fe_4Se_4(SeC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]$ ([4FeSSe]/GC, [4FeSeS]/GC, and [4FeSeSe]/GC, respectively) also exhibit the similar pH dependence as that of [4FeSS]/GC in H_2O.

The redox reaction of the Fe_4S_4 cluster-modified electrode is accompanied by the transport of the counter ion of the cluster between the redox center on the GC plate and the contacting aqueous electrolyte solutions. The migration of the counter ion of the cluster for the charge neutrality, therefore, largely influences the stability of the cluster modified electrodes. For example, the cyclic voltammogram of a glassy carbon plate modified with $(Et_4N)_4[Fe_4S_4(SC_6H_5)_4]$ was essentially consistent with that with the [4FeSS]/GC (Fig. 1). The anodic wave of the former, however, was almost disappeared in the multi-scanning cyclic voltammogram for 30 min, while the decrease in the anodic peak current of the glassy carbon electrode modified with $(Bu_4N)_2[Fe_4S_4(SC_6H_5)_4]$ was about 20% in the multi-scanning cyclic voltammogram for 1 h. Thus, a bulky counter ion of the cluster stabilizes the modified electrode. In addition, the Bu_4N^+ salt of the Fe_4S_4 cluster with the terminal ligand $SC_6H_4\text{-}p\text{-}t\text{-}Bu$ in place of SC_6H_5 further improved the stability of the cluster-modified electrode, as described in a previous section. It should be mentioned that the cyclic voltammogram of the Fe_4S_4 cluster-modified electrode did not show any redox couple of the cluster in the case a bulky Bu_4NClO_4 was used as an electrolyte in pure H_2O.[14] This fact clearly indicates that the charge neutrality in the [4FeXY]/GC (X, Y=S, Se) is maintained by the transport of Na^+ from the aqueous NaOH–H_3PO_4 buffer solution rather than that by H^+.[15] If the diffusion coefficient of Na^+ in the [4FeXY]/GC is assumed to be constant in the experimental pH region, the pH dependent cyclic voltammogram of [4FeXY]/GC (see Fig. 1a and 1b) is ascribed to the change of the proton concentrations in the aqueous phase. In accordance with this, not only oxidized but also reduced species of the current clusters undergo reversible protonation reactions in aqueous Triton X-100 micellar and poly[2-(dimethylamino)hexanamide] (PDACA) solutions.[9] The pH dependent redox behavior of the [4FeXY]/GC, therefore, also can be associated with such the reversible protonation of the clusters modified on the GC plate.

Not only the pattern of the cyclic voltammogram but also the peak potentials of the $[4FeXY]^{2-/3-}$ redox couples are altered by the change of proton concentrations in the aqueous phase. The anodic and cathodic peak potentials (E_{pa} and E_{pc}, respectively) of the [4FeXY]/GC at various pH, therefore, are depicted in Fig. 2, where E_{pa} and E_{pc} were determined at the sweep rate 10 mV s^{-1} in order to minimize the effect of the sweep rate on those peak potentials.[16] Although the E_{pc} value in the neutral pH region was not determined accurately due to the cathodic current of the H_2 evolution, the dependence of the E_{pc} values on pH is consistent with that of the E_{pa} on pH; the E_{pa} and E_{pc} values of the [4FeSS]/GC and the [4FeSeS]/GC show a tendency to level off in the pH region lower and higher than around 9.5 and 10.5, respectively and a shift by −60 mV/pH in the intermediate pH region (Fig. 2a).

Such the characteristic curves of Fig. 2a can be explained in terms of the reversible protonation of not only $[4FeXS]^{2-}$ but also $[4FeXS]^{3-}$ (X=S, Se) modified on the GC plate as similar to that of those clusters solubilized in an aqueous PDACA solution.9) The turning points of Fig. 2a can, therefore, be associated with the pK_a values of the cluster. From the consideration of the basicity of $[4FeXS]^{2-}$ and $[4FeXS]^{3-}$, the protonation of $[4FeXS]^{3-}$ should take place in higher pH region than that of $[4FeXS]^{2-}$. The turning points in the plots of E_{pa} vs. pH (or E_{pc} vs. pH) around pH 10.5 and 9.5 in Fig. 2a, therefore, are assigned to the pK_a^{red} and pK_a^{ox} values of the protonated (3−) and (2−) states of the clusters, respectively. The shift of the E_{pa} and E_{pc} values of the [4FeXS]/GC by −60 mV/pH in the pH region from the pK_a^{red} to pK_a^{ox} values, therefore, is caused by the dissociation of one proton upon the oxidation of the protonated $[4FeXY]^{3-}$ to $[4FeXY]^{2-}$, and the association of one proton to $[4FeXY]^{3-}$ formed by the reduction of $[4FeXY]^{2-}$. On the basis of the preceding discussion, the turning points observed at around 10.5 (Fig. 2b) in the plots of E_{pa} and E_{pc} values of the [4FeXSe]/GC (X=S, Se) against pH can be assigned to their pK_a^{ox} values. The continuous shift by −60 mV/pH of the E_{pa} and E_{pc} values of those clusters above pH 10.5, therefore, is reasonably explained by the pK_a^{red} values of the protonated $[4FeXSe]^{3-}$ (X=S, Se) being larger than 12. It should be noticed that the relation between E_{pa} and E_{pc} of the cluster and pH affords only the information about the difference in the number of protons attached to the (2−) and (3−) states of the cluster. The total number of protons bonded to $[4FeXY]^{2-}$ and $[4FeXY]^{3-}$ is not clear in the present study so that the protonation equilibriums of [4FeXY]/GC are depicted by Scheme 1, where n, E_1, E_2 are the total number of protons bonded to the clusters in a given pH, the redox potential of the $[4FeXY]^{2-/3-}(H^+)_{n-1}$, and that of the $[4FeXY]^{2-/3-}\ (H^+)_n$.17)

Table 1 summarizes the pK_a^{red} and pK_a^{ox} of the [4FeXY]/GC obtained from the turning points of the plots of E_{pa}^{ox} vs. pH of Fig. 2 together with those values determined in an aqueous PDACA solution.9) Although the pK_a^{red} values of the protonated $[4FeXSe]^{3-}$ could not be determined in the present study, the pK_a^{ox} values are divided into two groups; around 9.5 for $[4FeSS]^{2-}$ and $[4FeSeS]^{2-}$, and around 10.5 for $[4FeSSe]^{2-}$



Scheme 1.

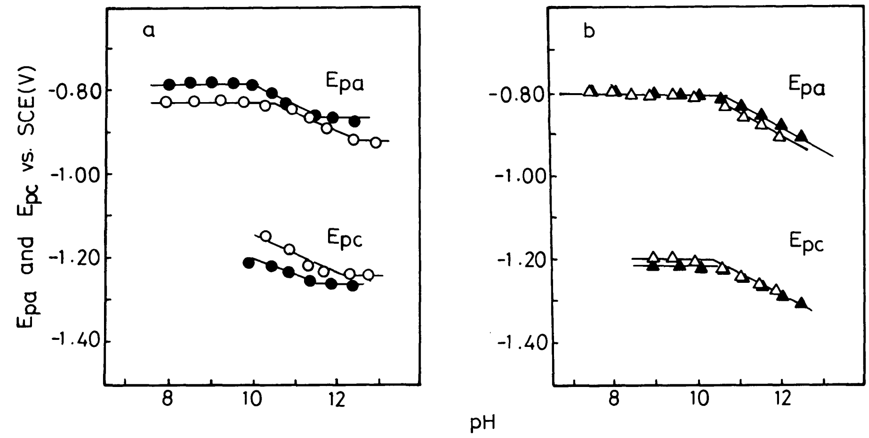


Fig. 2. Plots of peak potentials of the anodic and cathodic waves of the $[4FeXY]^{2-/3-}$ redox couple; X,Y=S,S (○), SeS (●), SSe (△), and SeSe (▲).

Table 1. pK_a Values of the Oxidized and Reduced Cluster Modified on a Glassy Carbon Plate and Solubilized in an Aqueous PDACA Solution

Cluster	pK_a^{ox}	pK_a^{red}
$[Fe_4S_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{2-}$	9.6 (5.9)a)	11.4 (8.8)
$[Fe_4Se_4(SC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{2-}$	9.2 (5.9)	10.5 (7.3)
$[Fe_4S_4(SeC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{2-}$	10.4 (6.9)	(8.8)
$[Fe_4Se_4(SeC_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{2-}$	10.6 (6.7)	(7.3)

a) Values in parentheses are in a PDACA solution.9) and $[4FeSeSe]^{2-}$. Such a pK_a^{ox} difference may be explained in terms of the difference of terminal sulfur and selenium rather than that of the Fe_4X_4 core (X=S, Se), suggesting that the protonation of $[4FeXY]^{2-}$ modified on the glassy carbon plate takes place on the terminal sulfur or selenium atom. It is worthy to note that both pK_a^{red} and pK_a^{ox} values of the [4FeXY]/GC are fairly larger than those of the clusters solubilized in aqueous PDACA solution (values in parentheses in Table 1). This result suggests that the hydrophobicity around the cluster modified on the GC plates in H_2O is less than that in an aqueous PDACA solution.

Rate Constants of the Electron Transfer between Clusters and Glassy Carbon Plates. As described in a previous section, the electricity consumed in the anodic and cathodic waves of the [4FeSS]/GC at pH 11.4 is equal to the amount of $[4FeSS]^{2-}$ modified on the GC plates, while the electricity of the anodic wave at pH 8.4 is much smaller than the amount of $[4FeSS]^{2-}$ (Fig. 1). This discrepancy may result from the fact that the reduction of the cluster is followed by H_2 evolution catalyzed by the resultant $[4FeXY]^{3-}$. Even if all the clusters modified on the GC plate participate in the redox reaction, the agreement between the electricity consumed in those redox waves and the amount of $[4FeXY]^{2-}$ modified is realized only when the rate of the electron transfer (k_s) between the cluster and the GC plate is much faster than that of H_2 evolution, otherwise most of electrons transferred to $[4FeXY]^{2-}$ from the GC plates are consumed by H_2 evolution prior to the anodic process of $[4FeXY]^{3-}$ in the GC plate. Accordingly, in a case of k_s being slower than the rate of H_2 evolution, the electricity released in the anodic wave of the [4FeXY]/GC is smaller than the amount of $[4FeXY]^{2-}$ modified on the GC plate. The rate of H_2 evolution apparently increases with decreasing pH. The rate of the electron transfer in the [4FeXY]/GC was evaluated under the assumption that H_2 evolution catalyzed by the reduced cluster does not disturb seriously the rate of the electron transfer.

The values of the peak separation between anodic and cathodic waves (ΔE_p) of an adsorbed species is frequently used as the criterion for kinetics in the electron transfer between the electrode and the redox center. For rapid kinetics in the electron transfer, $\Delta E_p=0$ is expected at any scan rate.[18] The present clusters, however, shows a fairly large ΔE_p values (300—400 mV) even at sweep rate 10 mV s^{-1} (Fig. 1), and both E_{pa} and E_{pc} are dependent on sweep rates. In the present study, both oxidized and reduced clusters are attached to the GC plate. When a redox center in a modified electrode is distributed homogeneously without any special interaction with the neighboring one, the rate constant of electron transfer k_s is expressed by Eq. 2,[19]

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log \alpha - \log(RT/nFv) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \qquad (2)$$

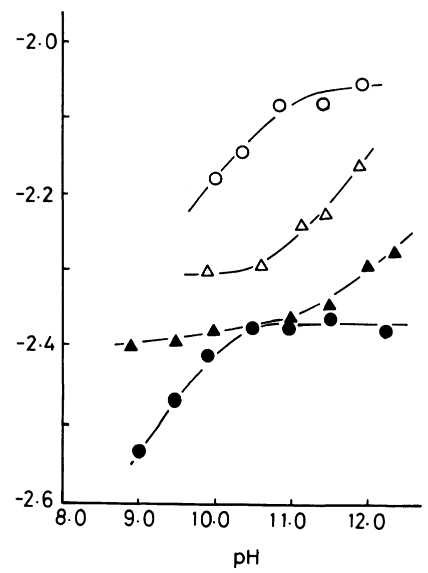


Fig. 3. The rate constant of the electron transfer (k_s) of the [4FeXY]/GC (X,Y=S,Se) at various pH; X,Y=S,S (○), SeS (●), SSe (△), and SeSe (▲).

where α, R, T, n, F, and v are the transfer coefficient, the gas constant, temperature, the Faraday constant, and the sweep rate. The value of α was obtained by the half width of the anodic wave (α=62.5 mV/$\delta_{1/2}$).[20] As mentioned in previous section, the cathodic wave of the (2−/3−) redox couple in the neutral region is almost completely concealed by H_2 evolution catalyzed by the (3−) state of the cluster, the k_s value, therefore, was determined in a limited pH region, where E_{pc} can be determined accurately. The plot of k_s obtained vs. pH is depicted in Fig. 3, which clearly shows the tendency of the decrease of k_s with increasing pH and the presence of the turning points close to the pK_a^{red} and pK_a^{ox} values of each [4FeXY]/GC (compare Fig. 2 with Fig. 3). Taking account the fact that protons in aqueous phase does not function as a counter ion in the redox reaction of the [4FeXY]/GC, the protonation of not only $[4FeXY]^{2-}$ but also $[4FeXY]^{3-}$ may cause a retardation of the rate of the electron transfer. Thus, the decrease of the electricity consumed in the anodic wave with decreasing pH (Fig. 1) may be caused by the retardation of the electron transfer, resulting from the protonation of the [4FeXY]/GC. It has been elucidated that the structure of $[Fe_4S_4(SC_6H_5)_4]^{2-}$ is nearly D_{2d} core symmetry with four short and eight longer Fe–S bonds approximately parallel to and perpendicular to the $\bar{4}$ axis,[21] while that of $[Fe_4S_4(SC_6H_5)_4]^{3-}$ is idealized D_{2d} core symmetry with four long Fe–S bonds approximately parallel to the $\bar{4}$ axis.[22] The similar structural change between $[4FeXY]^{2-}$ and $[4FeXY]^{3-}$ should be caused by the redox reaction of the [4FeXY]/GC. Such a reorganization process involved in the redox reaction of a Fe_4S_4 cluster may hardly influence on the rate of electron transfer in a certain Fe_4S_4 cluster-modified electrode since $[Fe_4S_4(SC_6H_5\text{-}p\text{-}n\text{-}C_8H_{17})_4]^{2-}$ adsorbed on an Hg electrode undergoes a similar protonation reaction in an aqueous lecithin vesicle solution and exhibits a reversible (2−/3−) redox couple with $\Delta E_p=0$ at any scan rates in neutral and weak acidic conditions.[23] The distinct difference in the rate of the electron transfer in the redox reactions between $[Fe_4S_4(SC_6H_5\text{-}p\text{-}n\text{-}C_8H_{17})_4]^{2-}$ adsorbed on an Hg electrode and $[Fe_4X_4(Y_4C_6H_4\text{-}p\text{-}t\text{-}Bu)_4]^{2-}$ (X, Y=S, Se) modified on a GC plate may be associated with the form of the cluster; the former exists as a monomeric form on the Hg electrode, while the latter exists as the solid form on the GC plate. The rate-determining step of the electron transfer in the present study may, therefore, involve the structural change of the cluster in the solid state. The agreement of the turning points in the plots of k_s vs. pH with the pK_a^{ox} and pK_a^{red} values of those clusters suggests that protonation of the [4FeXY]/GC increases the reoganization energy of the cluster in the solid state.

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13) In the case the amount of the cluster on the GC plate is more than 10^{-6} mol cm^{-2}, the electricity in the anodic wave of the [4FeSS]/GC is fairly smaller than the expected value even at pH 11.4 due to a poor conductivity of the cluster.

14) $(Bu_4N)_2$[4FeSS] is irreversibly oxidized around 0 V vs. SCE in DMF. However, the [4FeSS]/GC showed no anodic wave at potentials more positive than 0 V vs. SCE in H_2O, since Bu_4N^+ may be completely fixed on the GC plate.

15) The reduction of $(Bu_4N)_2$[4FeSS] on the GC plate results in the formation of $(Bu_4N)_2Na$[4FeSS].

16) Both E_{pa} and E_{pc} values depend on the sweep rate, but the turning points of Fig. 2 is essentially independent on the sweep rates in the range of 10 to 100 mV s^{-1}.

17) The half wave potential for the overall electrode reaction can be written as follows;[9]

$$E_{1/2} = E^1_{1/2} + (RT/F)\ln[K_{ox}(K_{red} + [H]^+)/(K_{red}(K_{ox} + [H]^+))]$$

or

$$E_{1/2} = E^2_{1/2} + (RT/F)\ln[(K_{red} + [H]^+)/(K_{ox} + [H]^+)]$$

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20) E. Laviron, *J. Electroanal. Chem.*, **51**, 355 (1974); the value α was in the range 0.39 to 0.46 for the [4FeSS]/GC, 0.38 to 0.42 for the [4FeSSe]/GC, 0.42 to 0.50 for the [4FeSeS]/GC, and 0.38 to 0.43 for the [4FeSeSe]/GC. No clear relation between these values and pH was observed.

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